US008193381B2

(12) **United States Patent**
Lilga et al.

(10) **Patent No.: US 8,193,381 B2**
(45) **Date of Patent: Jun. 5, 2012**

(54) **HYDROXYMETHYL FURFURAL OXIDATION METHODS**

(75) Inventors: **Michael A. Lilga**, Richland, WA (US); **Richard T. Hallen**, Richland, WA (US); **Jianli Hu**, Overland Park, KS (US); **James F. White**, Richland, WA (US); **Michel J. Gray**, Pasco, WA (US)

(73) Assignee: **Battelle Memorial Institute**, Richland, WA (US)

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 68 days.

(21) Appl. No.: **12/712,095**

(22) Filed: **Feb. 24, 2010**

(65) **Prior Publication Data**

US 2010/0152469 A1 Jun. 17, 2010

Related U.S. Application Data

(62) Division of application No. 11/932,436, filed on Oct. 31, 2007, now Pat. No. 7,700,788.

(60) Provisional application No. 60/863,704, filed on Oct. 31, 2006.

(51) **Int. Cl.**
C07D 307/02 (2006.01)
C07D 307/48 (2006.01)

(52) **U.S. Cl.** **549/485**; 549/489

(58) **Field of Classification Search** 549/483, 549/484, 485, 488, 489

See application file for complete search history.

(56) **References Cited**

U.S. PATENT DOCUMENTS

3,326,944	A *	6/1967	Lew	549/485
4,549,025	A	10/1985	Dalcanale et al.	
4,897,497	A	1/1990	Fitzpatrick	
4,977,283	A *	12/1990	Leupold et al.	549/484
5,608,105	A	3/1997	Fitzpatrick	
5,892,107	A	4/1999	Farone et al.	
6,706,900	B2	3/2004	Grushin et al.	
6,790,997	B2	9/2004	Eckert et al.	
7,956,203	B2	6/2011	Grushin et al.	
2003/0055271	A1	3/2003	Grushin et al.	

FOREIGN PATENT DOCUMENTS

DE	3826073	A1	7/1988
EP	0356703	A	3/1990
FR	2669636	A1	5/1992
GB	2188927	A	10/1987

(Continued)

OTHER PUBLICATIONS

Verdeguer et al, Catalytic Oxidation of HMF into furan-2,5-dicarboxylic acid, Journal of Molecular Catalysis , 1993, p. 327-344. translated.*

(Continued)

Primary Examiner — Taylor Victor Oh

(74) *Attorney, Agent, or Firm* — Wells St. John P.S.

(57) **ABSTRACT**

A method of oxidizing hydroxymethylfurfural (HMF) includes providing a starting material which includes HMF in a solvent comprising water into a reactor. At least one of air and O_2 is provided into the reactor. The starting material is contacted with the catalyst comprising Pt on a support material where the contacting is conducted at a reactor temperature of from about 50° C. to about 200° C. A method of producing an oxidation catalyst where ZrO_2 is provided and is calcined. The ZrO_2 is mixed with platinum (II) acetylacetonate to form a mixture. The mixture is subjected to rotary evaporation to form a product. The product is calcined and reduced under hydrogen to form an activated product. The activated product is passivated under a flow of 2% O_2.

15 Claims, 39 Drawing Sheets